

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : A61K 7/06		A1	(11) International Publication Number: WO 99/44567 (43) International Publication Date: 10 September 1999 (10.09.99)
(21) International Application Number: PCT/EP99/00321			(74) Agent: GRIFFITHS, Helen, Sarah; Unilever PLC, Patent Dept., Colworth House, Shambrook, Bedford MK44 1LQ (GB).
(22) International Filing Date: 19 January 1999 (19.01.99)			
(30) Priority Data: 9804725.1	5 March 1998 (05.03.98)	GB	(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
<p>(71) Applicant (for AU BB CA CY GB GD GH GM IE IL KE LC LK LS MN MW NZ SD SG SL SZ TT UG ZW only): UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB).</p> <p>(71) Applicant (for all designated States except AU BB CA CY GB GD GH GM IE IL IN KE LC LK LS MN MW NZ SD SG SL SZ TT UG ZW): UNILEVER N.V. [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).</p> <p>(71) Applicant (for IN only): HINDUSTAN LEVER LIMITED [IN/IN]; Hindustan Lever House, 165/166 Backbay Reclamation, Mumbai 400 020, Maharashtra (IN).</p> <p>(72) Inventor: MURRAY, Andrew, Malcom; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside L63 3JW (GB).</p>			
<p>(54) Title: SHAMPOO COMPOSITIONS CONTAINING SILICONE</p> <p>(57) Abstract</p> <p>Improved conditioning performance from a surfactant-based shampoo composition can be achieved by the inclusion in the shampoo composition of a specific combination of silicones, namely amino functionalised silicone and high viscosity non-amino functionalised silicone. Accordingly, the invention provides an aqueous shampoo composition comprising, in addition to water: i) at least one surfactant chosen from anionic, nonionic, zwitterionic or amphoteric surfactants or mixtures thereof; ii) an amino functionalised silicone; and iii) emulsified particles of an insoluble, non-amino functionalised silicone, in which the viscosity of the silicone itself is at least 500,000 cst, preferably at least 1,000,000 cst.</p>			

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

- 1 -

SHAMPOO COMPOSITIONS CONTAINING SILICONE

5 FIELD OF THE INVENTION

This invention relates to shampoo compositions, and more particularly to shampoo compositions containing emulsified particles of silicone, which compositions condition the hair
10 leaving it softer and more manageable.

BACKGROUND AND PRIOR ART

The use of silicones as conditioning agents in cosmetic
15 formulations is well known and widely documented in the patent literature. Generally, dispersed droplets of the silicone oil are suspended in the composition, which is then applied to the hair to deposit the silicone material on the hair shaft..

20 A problem encountered with silicone shampoo formulations is that the conditioning performance may be insufficient for many people, particularly in regions such as Japan and South East Asia where consumers desire a high level of
25 conditioning and a "weighty" feel to their hair.

We have now found that improved conditioning performance from a surfactant-based shampoo composition can be achieved by the inclusion in the shampoo composition of a specific
30 combination of silicones, namely amino functionalised silicone and high viscosity non-amino functionalised silicone.

- 2 -

US 5,198,209 (Amway Corp) published 1993 discloses a conditioning shampoo with cleansing surfactant and a combination of dimethicone and trimethylsilylamodimethicone, and mentions that superior conditioning benefits are obtainable when an aminofunctional silicone is used with polyalkylsiloxane (e.g. dimethicone) or polyalkylarylsiloxane. For optimum conditioning the viscosity of the dimethicone is said to range from 30,000 to 100,000 cst.

10

L'Oreal EP 0 811 371 describes cleansing compositions for hair comprising surfactant and a conditioning system comprising (i) cationic polymer (ii) aminofunctional silicone (iii) insoluble non-aminofunctional silicone of viscosity less than or equal to 100,000 cst. The composition is said to improve wet and dry combing, manageability, softness and smoothness. This document specifically teaches against replacing 60,000 cst dimethicone with 300,000 cst dimethicone in a composition comprising amodimethicone.

SUMMARY OF THE INVENTION

The invention provides an aqueous shampoo composition comprising, in addition to water:

- i) at least one surfactant chosen from anionic, nonionic, zwitterionic or amphoteric surfactants or mixtures thereof;
- 30 ii) an amino functionalised silicone; and
- iii) emulsified particles of an insoluble, non-amino functionalised silicone, in which the viscosity of the

- 3 -

silicone itself is at least 500,000 cst, preferably at least 1,000,000 cst.

DETAILED DESCRIPTION OF THE INVENTION

5

Surfactant

The composition according to the invention comprises a surfactant chosen from anionic, nonionic, zwitterionic or 10 amphoteric surfactants or mixtures thereof.

Suitable anionic surfactants include the alkyl sulphates, alkyl ether sulphates, alkaryl sulphonates, alkanoyl isethionates, alkyl succinates, alkyl sulphosuccinates, N-15 alkoyl sarcosinates, alkyl phosphates, alkyl ether phosphates, alkyl ether carboxylates, and alpha-olefin sulphonates, especially their sodium, magnesium ammonium and mono-, di- and triethanolamine salts. The alkyl and acyl groups generally contain from 8 to 18 carbon atoms and may 20 be unsaturated. The alkyl ether sulphates, alkyl ether phosphates and alkyl ether carboxylates may contain from one to 10 ethylene oxide or propylene oxide units per molecule, and preferably contain 2 to 3 ethylene oxide units per molecule.

25

Examples of suitable anionic surfactants include sodium oleyl succinate, ammonium lauryl sulphosuccinate, ammonium lauryl sulphate, sodium dodecylbenzene sulphonate, triethanolamine dodecylbenzene sulphonate, sodium cocoyl 30 isethionate, sodium lauroyl isethionate and sodium N-lauryl sarcosinate. The most preferred anionic surfactants are sodium lauryl sulphate, triethanolamine lauryl sulphate, triethanolamine monolauryl phosphate, sodium lauryl ether

- 4 -

sulphate 1EO, 2EO and 3EO, ammonium lauryl sulphate and ammonium lauryl ether sulphate 1EO, 2EO and 3EO.

Nonionic surfactants suitable for use in compositions of the 5 invention may include condensation products of aliphatic (C₈-C₁₈) primary or secondary linear or branched chain alcohols or phenols with alkylene oxides, usually ethylene oxide and generally having from 6 to 30 ethylene oxide groups. Other suitable nonionics include mono- or di-alkyl alkanolamides. 10 Example include coco mono- or di- ethanolamide and coco mono-isopropanolamide.

Amphoteric and zwitterionic surfactants suitable for use in compositions of the invention may include alkyl amine 15 oxides, alkyl betaines, alkyl amidopropyl betaines, alkyl sulphobetaines (sultaines), alkyl glycimates, alkyl carboxyglycimates, alkyl amphopropionates, alkylamphoglycimates alkyl amidopropyl hydroxysultaines, acyl taurates and acyl glutamates, wherein the alkyl and 20 acyl groups have from 8 to 19 carbon atoms. Examples include lauryl amine oxide, cocodimethyl sulphopropyl betaine and preferably lauryl betaine, cocamidopropyl betaine and sodium cocamphopropionate.

25 Generally, the surfactants are present in shampoo compositions of the invention in an amount of from 0.1 to 50%, preferably from 5 to 30%, more preferably from 10% to 25% by weight.

30 Amino functionalised silicone

- 5 -

By "amino functionalised silicone" is meant a silicone containing at least one primary, secondary or tertiary amine group, or a quaternary ammonium group.

5 Examples include:

(i) polysiloxanes having the CTFA designation "amodimethicone", and the general formula:

10 $\text{HO-[Si(CH}_3)_2-\text{O-]}_x-\text{[Si(OH)(CH}_2\text{CH}_2\text{CH}_2\text{-NH-CH}_2\text{CH}_2\text{NH}_2)-\text{O-]}_y\text{-H}$

in which x and y are numbers depending on the molecular weight of the polymer, generally such that the molecular weight is between about 5,000 and 500,000.

15

(ii) polysiloxanes having the general formula:

$\text{R}'_a\text{G}_{3-a}\text{-Si(OSiG}_2)_n\text{-}(\text{OSiG}_b\text{R}'_{2-b})_m\text{-O-SiG}_{3-a}\text{-R}'_a$

20 in which:

G is selected from H, phenyl, OH or C₁₋₈ alkyl, e.g. methyl; a is 0 or an integer from 1 to 3, preferably 0;

b is 0 or 1, preferably 1;

25 m and n are numbers such that (m + n) can range from 1 to 2000, preferably from 50 to 150;

m is a number from 1 to 2000, preferably from 1 to 10;

n is a number from 0 to 1999, preferably from 49 to 149, and

30 R' is a monovalent radical of formula -C_qH_{2q}L in which q is a number from 2 to 8 and L is an aminofunctional group selected from the following:

- 6 -

$-\text{NR}''-\text{CH}_2-\text{CH}_2-\text{N}(\text{R}'')_2$
 $-\text{N}(\text{R}'')_2$
 $-\text{N}^+(\text{R}'')_3\text{A}^-$
5 $-\text{N}^+\text{H}(\text{R}'')_2\text{A}^-$
 $-\text{N}^+\text{H}_2(\text{R}'')\text{A}^-$
 $-\text{N}(\text{R}'')-\text{CH}_2-\text{CH}_2-\text{N}^+\text{H}_2(\text{R}'')\text{A}^-$

in which R'' is selected from H, phenyl, benzyl, or a
10 saturated monovalent hydrocarbon radical, e.g. C_{1-20} alkyl,
and
A is a halide ion, e.g. chloride or bromide.

Suitable amino functionalised silicones corresponding to the
15 above formula include those polysiloxanes termed
"trimethylsilylamodimethicone" as depicted below, and which
are sufficiently water insoluble so as to be useful in
compositions of the invention:

20 $\text{Si}(\text{CH}_3)_3 - \text{O} - [\text{Si}(\text{CH}_3)_2 - \text{O} -]_x - [\text{Si}(\text{CH}_3)(\text{R} - \text{NH} -$
 $\text{CH}_2\text{CH}_2\text{NH}_2) - \text{O} -]_y - \text{Si}(\text{CH}_3)_3$

wherein $x + y$ is a number from about 50 to about 500, and
wherein R is an alkylene group having from 2 to 5 carbon
25 atoms. Preferably, the number $x + y$ is in the range of from
about 100 to about 300.

(iii) quaternary silicone polymers having the general
formula:

30 $\{(\text{R}^1)(\text{R}^2)(\text{R}^3)\text{N}^+\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{O}(\text{CH}_2)_3[\text{Si}(\text{R}^4)(\text{R}^5)-\text{O}-]_n-\text{Si}(\text{R}^6)(\text{R}^7)-$
 $(\text{CH}_2)_3-\text{O}-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{N}^+(\text{R}^8)(\text{R}^9)(\text{R}^{10})\}(\text{X}^-)_2$

- 7 -

wherein R¹ and R¹⁰ may be the same or different and may be independently selected from H, saturated or unsaturated long or short chain alk(en)yl, branched chain alk(en)yl and C₅-C₈ 5 cyclic ring systems;

R² thru' R⁹ may be the same or different and may be independently selected from H, straight or branched chain lower alk(en)yl, and C₅-C₈ cyclic ring systems;

10 n is a number within the range of about 60 to about 120, preferably about 80, and

15 X⁻ is preferably acetate, but may instead be for example halide, organic carboxylate, organic sulphonate or the like.

Suitable quaternary silicone polymers of this class are described in EP-A-0 530 974.

20 Amino functional silicones suitable for use in the invention will typically have a mole % amine functionality in the range of from about 0.1 to about 8.0 mole %, preferably from about 0.1 to about 5.0 mole %, most preferably from about 0.1 to about 2.0 mole %. In general the amine concentration 25 should not exceed about 8.0 mole % since we have found that too high an amine concentration can be detrimental to total silicone deposition and therefore conditioning performance.

30 The viscosity of the amino functional silicone is not particularly critical and can suitably range from about 100 to about 500,000 cst.

- 8 -

Specific examples of amino functional silicones suitable for use in the invention are the aminosilicone oils DC2-8220, DC2-8166, DC2-8466, and DC2-8950-114 (all ex Dow Corning), and GE 1149-75, (ex General Electric Silicones).

5

Also suitable are emulsions of amino functional silicone oils with non ionic and/or cationic surfactant.

10 Suitably such pre-formed emulsions will have an average amino functional silicone particle size in the shampoo composition of less than 30, preferably less than 20, more preferably less than 10 microns. We have found that reducing the particle size generally improves conditioning performance. Most preferably the average amino functional 15 silicone particle size is less than 2 microns, ideally it ranges from 0.01 to 1 micron. Silicone emulsions having an average silicone particle size of \leq 0.15 microns are generally termed microemulsions.

20 Particle size may be measured by means of a laser light scattering technique, using a 2600D Particle Sizer from Malvern Instruments.

25 Pre-formed emulsions of amino functionalised silicone are available from suppliers of silicone oils such as Dow Corning and General Electric. Specific examples include DC929 Cationic Emulsion, DC939 Cationic Emulsion, DC949 Cationic emulsion, and the non-ionic emulsions DC2-7224, DC2-8467 and DC2-8154 (all ex Dow Corning).

30

An example of a quaternary silicone polymer useful in the present invention is the material K3474, ex Goldschmidt.

- 9 -

Emulsified, non-amino functionalised silicone

The shampoo composition of the invention comprises a non-amino functionalised silicone. The silicone is insoluble in 5 the aqueous matrix of the shampoo composition and so is present in an emulsified form, with the silicone present as dispersed particles.

We have found that enhanced conditioning performance can be 10 achieved through the usage in shampoo compositions of the invention of emulsified non-amino functional silicone of high viscosity. The viscosity of the silicone itself (not the emulsion or the final shampoo composition) is at least 500,000 cst. The viscosity of the silicone itself is 15 suitably at least 1 million cst. Preferably the viscosity does not exceed 10⁹ cst for ease of formulation. Viscosity can be measured by means of a glass capillary viscometer as set out further in Dow Corning Corporate Test Method CTM004 July 20 1970.

20 Suitable silicones include polydiorganosiloxanes, in particular polydimethylsiloxanes which have the CTFA designation dimethicone. Also suitable for use in shampoo compositions of the invention are polydimethyl siloxanes 25 having hydroxyl end groups, which have the CTFA designation dimethiconol. Also suitable for use in shampoos of the invention are silicone gums having a slight degree of cross-linking, as are described for example in WO 96/31188. These materials can impart body, volume and stylability to hair, 30 as well as good wet and dry conditioning.

Various methods of making emulsions of particles of silicones for use in the invention are available and are

- 10 -

well known and documented in the art. For example, emulsions may be prepared by high shear mechanical mixing of the silicone and water, or by emulsifying the silicone with water and an emulsifier (mixing the silicone into a heated 5 solution of the emulsifier for instance), or by a combination of mechanical and chemical emulsification. A further suitable technique for preparation of emulsions of particles of silicones is emulsion polymerisation. Emulsion polymerised silicones as such are described in US 2 891 820 10 (Hyde), US 3 294 725 (Findlay) and US 3 360 491 (Axon).

Emulsified non-amino functional silicones for use in shampoo compositions of the invention will also typically have an average silicone particle size in the shampoo composition of 15 less than 30, preferably less than 20, more preferably less than 10 microns. Again, we have found that reducing the particle size generally improves conditioning performance. Most preferably the average silicone particle size of the emulsified non-amino functional silicone in the shampoo 20 composition is less than 2 microns, ideally it ranges from 0.01 to 1 micron.

Particle size may be measured by means of a laser light scattering technique, using a 2600D Particle Sizer from 25 Malvern Instruments.

Suitable silicone emulsions for use in the invention are commercially available in a pre-emulsified form. This is particularly preferred since the pre-formed emulsion can be 30 incorporated into the shampoo composition by simple mixing. Pre-formed emulsions are available from suppliers of silicone oils such as Dow Corning, General Electric, Union

- 11 -

Carbide, Wacker Chemie, Shin Etsu, Toshiba, Toyo Beauty Co, and Toray Silicone Co.

Examples of suitable pre-formed emulsions include emulsions 5 DC2-1766 and DC2-1784 available from Dow Corning. These are both emulsions of dimethiconol in which the viscosity of the silicone itself is about 1 million cst. Cross-linked 10 silicone gums are also available in a pre-emulsified form, which is advantageous for ease of formulation. A preferred example is the material available from Dow Corning as DC X2- 1787, which is an emulsion of cross-linked dimethiconol gum in which the viscosity of the silicone itself is about 8×10^7 cst. A further preferred example is the material 15 available from Dow Corning as DC X2-1391, which is a microemulsion of cross-linked dimethiconol gum in which the viscosity of the silicone itself is about 1 million cst.

Silicone Ratios

20 The weight ratio of amino functionalised silicone to non-amino functionalised silicone is generally 1:2 or less. Suitably, the ratio of amino functionalised silicone to non-amino functionalised silicone ranges from 1:2 to 1:20, preferably 1:3 to 1:20, more preferably 1:3 to 1:8, 25 optimally around 1:4.

Silicone Levels

30 The total amount of silicone (amino functional and non-amino functional) incorporated into the shampoo compositions of the invention depends on the level of conditioning desired and the material used. A preferred amount is from 0.01 to about 10% by weight of the total composition although these

- 12 -

limits are not absolute. The lower limit is determined by the minimum level to achieve conditioning and the upper limit by the maximum level to avoid making the hair and/or skin unacceptably greasy.

5

We have found that a total amount of silicone of from 0.3 to 5%, preferably 0.5 to 3%, by weight of the total composition is a suitable level.

10 Cationic Deposition Polymer

A cationic deposition polymer is a preferred ingredient in shampoo compositions of the invention, for enhancing conditioning performance of the shampoo. By "deposition polymer" is meant an agent which enhances deposition of the silicone component from the shampoo composition onto the intended site during use, i.e. the hair and/or the scalp.

20 The deposition polymer may be a homopolymer or be formed from two or more types of monomers. The molecular weight of the polymer will generally be between 5 000 and 10 000 000, typically at least 10 000 and preferably in the range 100 000 to about 2 000 000. The polymers will have cationic nitrogen containing groups such as quaternary ammonium or 25 protonated amino groups, or a mixture thereof.

30 The cationic nitrogen-containing group will generally be present as a substituent on a fraction of the total monomer units of the deposition polymer. Thus when the polymer is not a homopolymer it can contain spacer non-cationic monomer units. Such polymers are described in the CTFA Cosmetic Ingredient Directory, 3rd edition. The ratio of the cationic

- 13 -

to non-cationic monomer units is selected to give a polymer having a cationic charge density in the required range.

Suitable cationic deposition polymers include, for example, 5 copolymers of vinyl monomers having cationic amine or quaternary ammonium functionalities with water soluble spacer monomers such as (meth)acrylamide, alkyl and dialkyl (meth)acrylamides, alkyl (meth)acrylate, vinyl caprolactone and vinyl pyrrolidine. The alkyl and dialkyl substituted 10 monomers preferably have C1-C7 alkyl groups, more preferably C1-3 alkyl groups. Other suitable spacers include vinyl esters, vinyl alcohol, maleic anhydride, propylene glycol and ethylene glycol.

15 The cationic amines can be primary, secondary or tertiary amines, depending upon the particular species and the pH of the composition. In general secondary and tertiary amines, especially tertiary, are preferred.

20 Amine substituted vinyl monomers and amines can be polymerized in the amine form and then converted to ammonium by quaternization.

25 The cationic deposition polymers can comprise mixtures of monomer units derived from amine- and/or quaternary ammonium-substituted monomer and/or compatible spacer monomers.

Suitable cationic deposition polymers include, for example: 30 - copolymers of 1-vinyl-2-pyrrolidine and 1-vinyl-3-methyl-imidazolium salt (e.g. chloride salt), referred to in the industry by the Cosmetic, Toiletry, and Fragrance

- 14 -

Association, (CTFA) as Polyquaternium-16. This material is commercially available from BASF Wyandotte Corp. (Parsippany, NJ, USA) under the LUVIQUAT tradename (e.g. LUVIQUAT FC 370);

5

- copolymers of 1-vinyl-2-pyrrolidine and dimethylaminoethyl methacrylate, referred to in the industry (CTFA) as Polyquaternium-11. This material is available commercially from Gaf Corporation (Wayne, NJ, USA) under the GAFQUAT 10 tradename (e.g., GAFQUAT 755N);

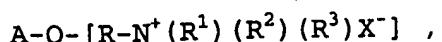
- cationic diallyl quaternary ammonium-containing polymers including, for example, dimethyldiallylammonium chloride homopolymer and copolymers of acrylamide and 15 dimethyldiallylammonium chloride, referred to in the industry (CTFA) as Polyquaternium 6 and Polyquaternium 7, respectively;

20 - mineral acid salts of amino-alkyl esters of homo-and co-polymers of unsaturated carboxylic acids having from 3 to 5 carbon atoms, (as described in U.S. Patent 4,009,256);

- cationic polyacrylamides (as described in WO95/22311).

25 Other cationic deposition polymers that can be used include cationic polysaccharide polymers, such as cationic cellulose derivatives, cationic starch derivatives, and cationic guar gum derivatives.

30 Cationic polysaccharide polymers suitable for use in compositions of the invention include those of the formula:



- 15 -

wherein: A is an anhydroglucose residual group, such as a starch or cellulose anhydroglucose residual. R is an alkylene, oxyalkylene, polyoxyalkylene, or hydroxyalkylene group, or combination thereof. R¹, R² and R³ independently 5 represent alkyl, aryl, alkylaryl, arylalkyl, alkoxyalkyl, or alkoxyaryl groups, each group containing up to about 18 carbon atoms. The total number of carbon atoms for each cationic moiety (i.e., the sum of carbon atoms in R¹, R² and R³) is preferably about 20 or less, and X is an anionic 10 counterion.

Cationic cellulose is available from Amerchol Corp. (Edison, NJ, USA) in their Polymer JR (trade mark) and LR (trade mark) series of polymers, as salts of hydroxyethyl cellulose 15 reacted with trimethyl ammonium substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 10. Another type of cationic cellulose includes the polymeric quaternary ammonium salts of hydroxyethyl cellulose reacted with lauryl dimethyl ammonium-substituted epoxide, referred 20 to in the industry (CTFA) as Polyquaternium 24. These materials are available from Amerchol Corp. (Edison, NJ, USA) under the tradename Polymer LM-200.

Other suitable cationic polysaccharide polymers include 25 quaternary nitrogen-containing cellulose ethers (e.g. as described in U.S. Patent 3,962,418), and copolymers of etherified cellulose and starch (e.g. as described in U.S. Patent 3,958,581).

30 A particularly suitable type of cationic polysaccharide polymer that can be used is a cationic guar gum derivative, such as guar hydroxypropyltrimonium chloride (Commercially

- 16 -

available from Rhodia (formerly Rhone-Poulenc) in their JAGUAR trademark series).

Examples are JAGUAR C13S and JAGUAR CB289, which have a low
5 degree of substitution of the cationic groups and high
viscosity. JAGUAR C15, having a moderate degree of
substitution and a low viscosity, JAGUAR C17 (high degree of
substitution, high viscosity), JAGUAR C16, which is a
hydroxypropylated cationic guar derivative containing a low
10 level of substituent groups as well as cationic quaternary
ammonium groups, and JAGUAR 162 which is a high transparency,
medium viscosity guar having a low degree of substitution.

Preferably the cationic deposition polymer is selected from
15 cationic cellulose and cationic guar derivatives.

Particularly preferred deposition polymers are JAGUAR C13S,
JAGUAR CB289, JAGUAR C15, JAGUAR C17 and JAGUAR C16 and
JAGUAR C162.

20 The cationic deposition polymer will generally be present at
levels of from 0.001 to 5%, preferably from about 0.01 to
1%, more preferably from about 0.02% to about 0.5% by weight
of the total composition.

25 Other Ingredients

The shampoo composition of the invention may further
comprise from 0.1 to 5 % by weight of the total composition
of a silicone suspending agent. Examples are polyacrylic
30 acids, cross linked polymers of acrylic acid, copolymers of
acrylic acid with a hydrophobic monomer, copolymers of
carboxylic acid- containing monomers and acrylic esters,
cross-linked copolymers of acrylic acid and acrylate esters,

- 17 -

heteropolysaccharide gums and crystalline long chain acyl derivatives. The long chain acyl derivative is desirably selected from ethylene glycol stearate, alkanolamides of fatty acids having from 16 to 22 carbon atoms and mixtures 5 thereof. Ethylene glycol distearate and polyethylene glycol 3 distearate are preferred long chain acyl derivatives. Polyacrylic acid is available commercially as Carbopol 420, Carbopol 488 or Carbopol 493. Polymers of acrylic acid cross-linked with a polyfunctional agent may also be used, 10 they are available commercially as Carbopol 910, Carbopol 934, Carbopol 940, Carbopol 941 and Carbopol 980. An example of a suitable copolymer of a carboxylic acid containing a monomer and acrylic acid esters is Carbopol 1342. All Carbopol materials are available from Goodrich 15 and Carbopol is a trade mark.

Suitable cross linked polymers of acrylic acid and acrylate esters are Pemulen TR1 or Pemulen TR2. A suitable heteropolysaccharide gum is xanthan gum, for example that 20 available as Kelzan mu.

Compositions of this invention may contain any other ingredient normally used in hair treatment formulations. These other ingredients may include viscosity modifiers, 25 preservatives, colouring agents, polyols such as glycerine and polypropylene glycol, chelating agents such as EDTA, antioxidants, fragrances, and sunscreens. Each of these ingredients will be present in an amount effective to accomplish its purpose. Generally these optional ingredients 30 are included individually at a level of up to about 5% by weight of the total composition.

- 18 -

Preferably, compositions of this invention also contain adjuvants suitable for hair care. Generally such ingredients are included individually at a level of up to 2%, preferably up to 1%, by weight of the total composition.

5

Among suitable hair care adjuvants, are:

(i) natural hair root nutrients, such as amino acids and sugars. Examples of suitable amino acids include arginine, 10 cysteine, glutamine, glutamic acid, isoleucine, leucine, methionine, serine and valine, and/or precursors and derivatives thereof. The amino acids may be added singly, in mixtures, or in the form of peptides, e.g. di- and tripeptides. The amino acids may also be added in the form 15 of a protein hydrolysate, such as a keratin or collagen hydrolysate. Suitable sugars are glucose, dextrose and fructose. These may be added singly or in the form of, e.g. fruit extracts. A particularly preferred combination of natural hair root nutrients for inclusion in compositions of 20 the invention is isoleucine and glucose. A particularly preferred amino acid nutrient is arginine.

(ii) hair fibre benefit agents. Examples are:

25 - ceramides, for moisturising the fibre and maintaining cuticle integrity. Ceramides are available by extraction from natural sources, or as synthetic ceramides and pseudoceramides. A preferred ceramide is Ceramide II, ex Quest. Mixtures of ceramides may also be suitable, such as 30 Ceramides LS, ex Laboratoires Serobiologiques.

The invention is further illustrated by way of the following non-limitative Example:

- 19 -

EXAMPLE

A shampoo composition was prepared by mixing the following components in the amounts stated:

5

Ingredient

		<u>% wt</u>
10	Sodium lauryl sulphate (2EO)	14.0
	Cocamidopropyl betaine	2.0
	Non-amino functionalised silicone ⁽¹⁾	1.5
	Sodium chloride	1.5
	Amino-functionalised silicone ⁽²⁾	0.5
15	Carbopol 980 ⁽³⁾	0.4
	Jaguar C13S ⁽⁴⁾	0.1
	Preservative, perfume,	q.s.
	colour	
	Water	to 100.0

20

(1) Non-amino functionalised silicone was included as DC2-1784 from Dow Corning Ltd., an emulsion (50% a.i.) of dimethiconol (1 million cst, 0.5 micron particle size) in 25 anionic surfactant (TEA-dodecylbenzenesulfonate).

(2) Amino functionalised silicone was included as DC929 from Dow Corning Ltd., an emulsion (35% a.i.) of amodimethicone in cationic surfactant (tallowtrimonium 30 chloride) and nonionic surfactant (nonoxynol-10).

(3) Carbopol 980 is a cross-linked polyacrylate available from B F Goodrich.

- 20 -

(4) Jaguar C13S is guar hydroxypropyltrimonium chloride available from Rhodia (formerly Rhone-Poulenc)

Example 2 and Comparative Example A

5

Two shampoo compositions were made up having ingredients as shown in the following Table:

INGREDIENT	% weight	
	Comparative Example A	Example 2
Sodium lauryl ether sulphate (2EO)	14.0	14.0
Cocamidopropyl betaine	2.0	2.0
Jaguar C13S	0.1	0.1
Pearliser ⁽⁵⁾	6.0	6.0
Formalin	0.1	0.1
DC 949 ⁽⁶⁾	1.0	1.0
DC 200 (60,000cst) ⁽⁷⁾	2.0	---
X2-1766 ⁽⁸⁾	---	2.0
NaCl	0.9	0.9
H ₂ O	to 100	to 100

10

(5) EUPERLAN PK3000, ex Henkel

(6) An emulsion (35% a.i.) of aminoethylaminopropyl 15 dimethylsiloxane emulsified with alkyltrimethylammonium chloride and polyethoxylated tridecylalcohol, ex Dow Corning

(7) Dimethicone fluid, viscosity 60,000 cst, ex Dow Corning

- 21 -

⁽⁸⁾ An emulsion (60% a.i.) of dimethiconol (1 million cst, 0.5 micron particle size) in anionic surfactant (sodium lauryl sulphate), ex Dow Corning

5 The shampoos of Example 2 and Comparative Example A were subjected to a panellist evaluation for various wet and dry conditioning attributes. The panellist preferences are shown in the following Table:

Attribute	Example 2	Comparative Example A
<i>WET FEEL</i>		
smoothness	79	21
ease of comb	83	17
<i>DRY FEEL</i>		
smoothness	75	25
ease of comb	83	17
lack of fly-away	85	15

10

Clearly the composition of the invention (with high viscosity silicone and amino functionalised silicone) outperformed the composition of the Comparative Example over 15 all attributes tested.

CLAIMS

1. An aqueous shampoo composition comprising, in addition to water:

5

i) at least one surfactant chosen from anionic, nonionic, zwitterionic or amphoteric surfactants or mixtures thereof;

10

ii) an amino functionalised silicone; and

15

iii) emulsified particles of an insoluble, non-amino functionalised silicone, in which the emulsified non-amino functional silicone has a viscosity (of the silicone itself) of at least 500,000 cst.

15

2. A shampoo composition according to claim 1, in which the emulsified non-amino functional silicone has a viscosity (of the silicone itself) of at least 1 million cst.

20

3. A shampoo composition according to claim 1 or claim 2, in which the weight ratio of amino functionalised silicone (ii) to non-amino functionalised silicone (iii) is 1:2 or less.

25

4. A shampoo composition according to any preceding claim, in which the amino functional silicone has a mole % amine functionality in the range of from about 0.1 to about 8.0 mole %, preferably from about 0.1 to about 5.0 mole %, most preferably from about 0.1 to about 2.0 mole %.

30

5. A shampoo composition according to any preceding claim, in which the amino functional silicone is in the form of an emulsion of amino functional silicone oil with non ionic and/or cationic surfactant, and in which the average

- 23 -

particle size of the amino functional silicone in the shampoo composition is less than 2 microns, preferably from 0.01 to 1 micron.

- 5 6. A shampoo composition according to any preceding claim, in which the emulsified non-amino functional silicone has an average silicone particle size in the shampoo composition of less than 2 microns, preferably from 0.01 to 1 micron.
- 10 7. A shampoo composition according to any preceding claim, in which the total amount of silicone is from 0.3 to 5%, preferably 0.5 to 3%, by weight of the total shampoo composition.
- 15 8. A shampoo composition according to any preceding claim, further comprising from 0.001 to 5% by weight of the total shampoo composition of a cationic deposition polymer selected from cationic cellulose and cationic guar derivatives.

INTERNATIONAL SEARCH REPORT

Inte onet Application No
PCT/EP 99/00321

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A61K7/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 674 898 A (UNILEVER) 4 October 1995 (1995-10-04) claims 1,2,5,6 page 3, line 1-11 page 4, line 1-14 ---	1,5-8
X	WO 98 05296 A (UNILEVER) 12 February 1998 (1998-02-12) claims 1,5,8 page 7, line 6 - page 8, line 15 ---	1,5-8
X	US 5 085 857 A (E.S.REID, A.M.MURRAY) 4 February 1992 (1992-02-04) claims 1,5-7 column 3, line 30 - column 4, line 8 ---	1,5-8

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority, claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

26 July 1999

Date of mailing of the international search report

30/07/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.
Fax: (+31-70) 340-3016

Authorized officer

Peeters, J

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte	.onal Application No
PCT/EP 99/00321	

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP 674898	A 04-10-1995	BR	9501289 A	31-10-1995
		CA	2145474 A	01-10-1995
		JP	7277931 A	24-10-1995
WO 9805296	A 12-02-1998	AU	3767097 A	25-02-1998
		EP	0917454 A	26-05-1999
US 5085857	A 04-02-1992	AT	96013 T	15-11-1993
		AU	620746 B	20-02-1992
		AU	6772590 A	06-06-1991
		CA	2031382 A,C	05-06-1991
		DE	69004057 D	25-11-1993
		DE	69004057 T	17-02-1994
		DK	432951 T	27-12-1993
		EP	0432951 A	19-06-1991
		ES	2060070 T	16-11-1994
		IN	171189 A	15-08-1992
		JP	1997997 C	08-12-1995
		JP	4364111 A	16-12-1992
		JP	7017491 B	01-03-1995
		JP	4036226 A	06-02-1992
		JP	6062392 B	17-08-1994